

**FORMING INDIUM NITRIDE (InN) AND INDIUM GALLIUM NITRIDE (InGaN)
QUANTUM DOTS GROWN BY METAL-ORGANIC-VAPOR-PHASE-EPITAXY
(MOCVD).**

[0001] This is a divisional application under 37 C.F.R. § 1.53(b) of pending prior Application No. 09/963,616 filed on September 27, 2001, the entire contents of which are hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] This invention relates to optoelectronics devices and fabrication methods, particularly to light emitting diodes and laser diodes.

BACKGROUND OF THE INVENTION

[0003] Light emitting diodes are widely used in optical displays, traffic lights, data storage, communications, medical and many other applications.

[0004] The development of blue LEDs and laser diodes has attracted considerable research activity to the growth of group III-nitrides. The band gap of group III-nitrides can be varied to provide light over nearly the whole spectral range from near UV to red. Accordingly, group III-nitrides find use in active regions of these devices.

[0005] The growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys and quantum wells is extremely difficult mostly due to the trade-off between the epilayer quality and the amount of InN incorporation into the alloy. Growth at high temperatures of approximately 800°C typically results in high crystalline quality but the amount of InN in the solid is limited to low values because of the high volatility of indium. Lowering the growth temperature results in an increase in the indium content at the expense of reduced crystalline quality. The lattice mismatch and different thermal stability of the two constituents, InN and GaN, also complicate the growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$. The lattice mismatch can lead to a miscibility gap. [1] H. Ho and G. B. Stringfellow, Appl. Phys. Lett. 69, 2701 (1996)., which causes fluctuations of In content across the film. Singh and co-workers [2] [3] [4] R. Singh, D. Doppalapudi, T. D. Moustakas, and L. T. Romano, Appl. Phys. Lett. 70, 1089 (1997); R. Singh and T. D. Moustakas, Mater. Res. Soc. Symp. Proc. 395, 163 (1996); R. Singh, W. D. Herzog, D. Doppalapudi, M. S. Unlu, B. B. Goldberg, and T. D.

Moustakas, Mater. Res. Soc. Symp. Proc. 449, 185 (1997).] provided strong evidence of phase separation in InGa_N thick films grown by molecular beam epitaxy (MBE). Other researchers reported phase separation in thick InGa_N films grown by metalorganic chemical vapor deposition (MOCVD) [5][6]. Behbehani [7 Akihiro Wakahara, Takashi Tokuda, Xiao-Zhong Dang, Susumu Noda, and Akio Sasaki, Appl. Phys. Lett. **71**, 906, (1997); N. A. El-Masry, E. L. Piner, S. X. Liu, and S. M. Bedair Appl. Phys. Lett., **72**, 40, (1998).5][6]. Behbehani [M. K. Behbehani, E. L. Piner, S. X. Liu, N. A. El-Masry, and S. M. Bedair Appl. Phys. Lett. **75** 2202, (1999)7] reported the co-existence of phase-separation and ordering in In_xGa_{1-x}N with $x > 0.25$. Up to now, growth of InGa_N/Ga_N quantum wells (QW) with emission in the green is still a challenging task.

[0006] InGa_N is a very important material because it is used in the active layer of LEDs and laser diodes (LD), However, researchers have not reached consensus on the optical emission mechanism in In_xGa_{1-x}N/In_yGa_{1-y}N QWs. There are a few theories; one attributing emission to In-rich quantum dots (QDs), one attributing emission to the piezoelectric effect and another combining aspects of both. Indium-rich QDs can be formed by spinodal decomposition, Stranski-Krastanov (SK) growth mode, or using antisurfactants.

SUMMARY OF THE INVENTION

[0007] It is therefore an object of the present invention to provide an improved technique for the growth of self-organized InGa_N quantum dots.

[0008] It is another object of the invention to produce light emitting diodes capable of emitting blue and green light.

[0009] These objects are provided, according to the present invention, by indium iIndium-rich QDs which are embedded in In_xGa_{1-x}N/Ga_N or In_xGa_{1-x}N/In_yGa_{1-y}N single and multiple quantum wells. These QDs are triggered by the flow of trimethyl indium iindium (TMIn) or other indium iIndium precursors acting as antisurfactants on a non- growing surface.

[0010] The conventional method of growth of QW is the following:

[0011] First, growing a low temperature buffer and then a high temperature Ga_N layer, with the former usually performed in the range of 450°C to 600°C and the latter usually

performed in the range of 900°C to 1100°C, most typically at 1030°C. The temperature was next lowered to about 700°C to 800°C to grow the GaN or InGaN barrier followed by the growth of the quantum well.

[0012] In this invention, after the growth of the barrier, an appropriate amount of indium-precursor such as trimethyl indium (TMIn), or triethyl indium (TEIn) or ethyldimethyl indium (EDMIn), was flowed in the presence of ammonia. Indium atoms from indium-precursor aggregate at the atomic edges of the InGaN barriers to form the “seeds” for the subsequent growth of quantum dots. So long as these precursors are used, whether be it in MOCVD or chemical beam epitaxy (CBE), this invention is applicable.

[0013] In a preferred embodiment of the present invention, a group of

[0014] $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{In}_y\text{Ga}_{1-y}\text{N}$ single quantum wells (SQWs) were grown by MOCVD on (0001) sapphire substrates. MOCVD was performed using trimethyl gallium (TMGa), trimethyl indium (TMIn), and ammonia (NH_3) as precursors, and hydrogen (H_2) and/or nitrogen (N_2) as the carrier gases. Triethyl gallium (TEGa), ethyldimethyl gallium (EDMGa), triethyl indium (TEIn), ethyldimethyl indium (EDMIn) can also be used as group III precursors, while dimethylhydrazine ($\text{H}_2\text{N}_2(\text{CH}_3)_2$, 1,1 DMHy) is preferred as a N precursor. For this group of SQWs, a 2 μm thick undoped bulk GaN was first grown on a 250Å thick GaN buffer layer. The growth temperature was 530°C and 1030°C respectively for the GaN buffer and bulk layer. After deposition of the GaN bulk layer, the growth temperature was lowered down to about 700°C to 800°C for the deposition of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ barrier and the $\text{In}_y\text{Ga}_{1-y}\text{N}$ well. After the deposition of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ barrier wherein x ranges from 0 to 0.10, and prior to the growth of $\text{In}_y\text{Ga}_{1-y}\text{N}$ well, wherein y is greater than x, TMIn was flowed at a flow rate less than 100 $\mu\text{mol}/\text{min}$ for a short time varying from 2 to 5 seconds with TMGa flow switched off.

[0015] The well thickness was about 30Å. A high temperature cap layer was grown on the top of $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{In}_y\text{Ga}_{1-y}\text{N}$ SQW at temperatures in the range of from 800°C to 1030°C.

[0016] In the second embodiment of the present invention, the second group of SQWs was grown, the growth conditions are the same as the first except that before the growth of the InGaN barrier, a low temperature GaN layer was grown at the same

temperature as the growth temperature of the barrier and well so that no temperature ramping is needed for the subsequent growth.

[0017] According to the invention, it has been found that the photoluminescence from the first and second groups of SQWs are 488nm and 548nm respectively at the room temperature. The luminescence from the first and the second group are in the blue and green regions respectively, which are suitable for the fabrication of blue and green LEDs.

[0018] The amount of TMIn acting as antisurfactants and the duration of the TMIn flow are important for the growth of ~~indium~~ **iIndium**-rich QDs: too small a flow may not form enough "seeds" for the subsequent growth of the QDs, while too much flow will create ~~indium~~ **iIndium** droplets which are competing with the formation of ~~indiumrich~~ **iIndium-rich** QDs. At room temperature, the luminescence comes from these dots rather than from the wells. The quantum confinement effect of the QDs is the reason why QDs have very high efficiency of luminescence even at room temperature.

[0019] After the flowing of TMIn, which acts as antisurfactant, the subsequent flow of TMIn, TMGa and ammonia are also very important for the growth of QDs.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Fig.1 illustrates the growth of SQWs in the first embodiment.

[0021] Fig.2 is the room temperature photoluminescence from the single quantum wells of the first embodiment.

[0022] Fig.3 is the transmission electron microscopy (TEM) of the first group of single quantum wells.

[0023] Fig.4 illustrates the growth of SQWs in the second embodiment.

[0024] Fig.5 is the room temperature photoluminescence from single quantum wells of the second embodiment.

DETAILED DESCRIPTION OF THE INVENTION

[0025] The present invention is now described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the inventions are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein. Rather, the invention is defined

by the following claims. In the drawings, the thicknesses of layers and regions are exaggerated for clarity.

[0026] FIG. 1 illustrates first embodiments of the InGa_N/InGa_N quantum well structure which can be used for the blue and green LEDs. Referring now to FIG. 1, layer 1 is the substrate which can be sapphire, silicon carbide (SiC), zinc oxide (ZnO) or other substrates. Layer 2 is the low-temperature buffer. Layer 3 is the undoped GaN or Si-doped GaN grown at around 1030°C, doped at a concentration of $2 \times 10^{17} \text{ cm}^{-3}$ to $9 \times 10^{18} \text{ cm}^{-3}$. Layer 4 is the In_xGa_{1-x}N barrier wherein x ranges from 0 to 0.001, grown at a temperature from 700°C to 800°C. After the growth of layer 4, TMIn and ammonia were flowed to form “seeds” for the growth of indium rich QDs at the same growth temperature of layer 4. Layer 5 is the In_yGa_{1-y}N quantum well, wherein y is greater than x, grown at the same temperature of layer 4. Layer 6 is another In_xGa_{1-x}N barrier grown at the same temperature of layer 4. Layer 7 is the GaN cap grown in the range of 800°C to 1100°C. The typical thickness for each layer is 200 μm to 500 μm for layer 1, 20 nm to 40 nm for layer 2, 1 μm to 4 μm for layer 3, 2 nm to 10 nm for layer 4, 2 nm to 4 nm for layer 5, 2 nm to 10 nm for layer 6, and 10 nm to 1000 nm for layer 7.

[0027] Still continuing with the description of FIG. 1, layer 1 may be any material suitable for the growth of GaN, such as sapphire, SiC, ZnO, and other alternatives. Layer 2, the low temperature buffer, can also be a multi-layered AlGa_N/GaN buffer. Layer 3 can be undoped GaN, or GaN that is Si-doped to a concentration $2 \times 10^{17} \text{ cm}^{-3}$ to $9 \times 10^{18} \text{ cm}^{-3}$, or GaN that is Mg-doped GaN to a concentration $5 \times 10^{17} \text{ cm}^{-3}$ to $3 \times 10^{20} \text{ cm}^{-3}$. Layers 4 and 5 can be GaN and/or AlGa_N instead of InGa_N. Layer 7, the high temperature cap, can also be AlGa_N.

[0028] FIG. 2 shows the photoluminescence at room temperature of the first group QW in the first embodiment. The wavelength of the emission is 488nm, which is in the blue region. Also note the narrow full width at half maximum (FWHM) of the luminescence which makes the blue color “pure” to the naked eye. This method can be readily used in the growth and fabrication of blue LEDs.

[0029] FIG. 3 shows the transmission electron microscopy (TEM) picture of the SQW in the first embodiment. As can be seen clearly from the figure, the QDs, which manifest themselves as the dark contrasts in TEM picture, are located at the interface between layer

4 (the InGaN barrier) and the layer 5 (the well). The interface between layer 4 and layer 5 is sharp. As previously mentioned, after the deposition of the InGaN barrier, flowing TMIn and ammonia provides “seeds” for the subsequent growth of these dots. The flow rate and duration of TMIn are important for the formation of these dots; a flow rate of less than 100 $\mu\text{mol/min}$ and duration of 2 seconds to 5 seconds are preferred. These QDs have higher indium content than the well with typical difference of In content from 10 % to 60 %, and they emit light with longer wavelengths. In this case, the 488nm luminescence comes from these QDs instead of from the well.

[0030] Referring now to FIG. 4, layer 1 is the substrate, which is preferably sapphire, SiC or ZnO; layer 2 is the low-temperature buffer grown at about 450°C to 600°C; layer 3 is the undoped GaN or Si-doped GaN, grown at around 1030°C; layer 4 is a GaN or InGaN grown at the same temperature as the barrier and well; layer 5 is a $\text{In}_x\text{Ga}_{1-x}\text{N}$ barrier, wherein x ranges from 0.01 to 0.1 grown at about 700°C to 800°C; after the growth of layer 5, TMIn and ammonia were flowed to form “seeds” for the growth of indium rich QDs; layer 6 is the $\text{In}_y\text{Ga}_{1-y}\text{N}$ quantum well where y is greater than x; layer 7 is another $\text{In}_x\text{Ga}_{1-x}\text{N}$ barrier typically similar to layer 5; layer 8 is the GaN cap grown at temperatures in the range of between 800°C and 1030°C.

[0031] Still continuing with the description of FIG. 4, layer 1 may be any material suitable for the growth of GaN, such as sapphire, SiC, ZnO, and other alternatives with thickness of about 200 μm to 500 μm . Layer 2, the low temperature buffer which is about 20nm to 40nm thick, can also be a multi-layered AlGaIn/GaN buffer. Layer 3 can be undoped GaN, or Si-doped GaN to a concentration $2 \times 10^{17} \text{ cm}^{-3}$ to $9 \times 10^{18} \text{ cm}^{-3}$, or Mg doped GaN to a concentration $5 \times 10^{17} \text{ cm}^{-3}$ to $3 \times 10^{20} \text{ cm}^{-3}$, and its thickness ranges from 1 μm to 4 μm . Layer 4 can be GaN, InGaN or AlGaIn grown at the same temperature as the barrier and well with the thickness of about 5 nm to 30 nm; Layer 5 and 6 can be GaN instead of InGaN. Layer 8, the 10nm to 1000 nm thick cap, can also be AlGaIn.

[0032] FIG. 5, shows the photoluminescence of the SQW in the second embodiment at room temperature. The wavelength is 540 nm, which is in the green region. Thus, the method of the present invention can be readily used in the growth and fabrication of green LEDs.

[0033] The insertion of the layer 4 in FIG. 4 is important to extending the luminescence from 488nm to 540nm. Without being bound by any theory of the invention,

it is thought that the low temperature GaN layer (layer 4 in Fig.4) partially relaxes the compressive strain between the InGaN well and barrier. This relaxation of compressive strain can result in a red shift in the luminescence. Relaxation of the compressive strain can also enhance the InGaN phase separation according to Kaprov's [8]-**MRS Internet J Nitride Semicond. Res. 3, 16 (1998).**] theory, in which compressive strain can suppress the InGaN phase separation.

[0034] The relatively rough surface of the low-temperature (LT) GaN layer (layer 4 in FIG. 4) could help keep the impinging indium atoms, which come from the cracking of TMIn precursor, on the surface for a longer time, thereby increasing the indium incorporation which will also result in red-shifting of the luminescence.

[0035] Various articles of the scientific periodical and/or patent literature are cited throughout this application. Each of such articles is hereby incorporated by reference in its entirety and for all purposes by such citation.

REFERENCES

~~Various articles of the scientific periodical and/or patent literature are cited throughout this application. Each of such articles is hereby incorporated by reference in its entirety and for all purposes by such citation.~~

1. ~~Ho and G. B. Stringfellow, Appl. Phys. Lett. 69, 2701 (1996).~~
2. ~~R. Singh, D. Doppalapudi, T. D. Moustakas, and L. T. Romano, Appl. Phys. Lett. 70, 1089 (1997).~~
3. ~~R. Singh and T. D. Moustakas, Mater. Res. Soc. Symp. Proc. 395, 163 (1996).~~
4. ~~R. Singh, W. D. Herzog, D. Doppalapudi, M. S. Unlu, B. B. Goldberg, and T. D. Moustakas, Mater. Res. Soc. Symp. Proc. 449, 185 (1997).~~
5. ~~Akihiro Wakahara, Takashi Tokuda, Xiao Zhong Dang, Susumu Noda, and Akio Sasaki, Appl. Phys. Lett. 71, 906, (1997).~~
6. ~~N. A. El Masry, E. L. Piner, S. X. Liu, and S. M. Bedair Appl. Phys. Lett., 72, 40, (1998).~~
7. ~~M. K. Behbehani, E. L. Piner, S. X. Liu, N. A. El Masry, and S. M. Bedair Appl. Phys. Lett. 75 2202, (1999).~~
8. ~~MRS Internet J Nitride Semicond. Res. 3, 16 (1998).~~